

PATENT SPECIFICATION

(11) 1 526 398

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- (21) Application No. 52917/74 (22) Filed 6 Dec. 1974
- (23) Complete Specification Filed 5 Dec. 1975
- (44) Complete Specification Published 27 Sep. 1978
- (51) INT. CL.² C08J 3/24
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 C3P D9A7 D9B11 D9D7D1
 B5A 1G1 1G3X 1G5A 1G5E 2D1X 2L 1R130 1R314C12
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- (72) Inventors: Peter Swarbrick
 William John Green
 Charles Maillefer

(19)



PATENTS ACT 1949

SPECIFICATION NO 1526398

The following amendments were allowed under Section 29 on 14 May 1979

- Page 1, line 17 *after has insert in practice*
- Page 1, line 22 *after machine insert* having in succession a premixing zone, a homogenising zone of the kind in which the material to be extruded is forced over the flight of the extruder screw from a converging groove to another groove not otherwise communicating with the converging groove and a metering zone
- Page 1, line 25 *delete and insert in the mixing and homogenising zones and then*
- Page 1, line 26 *after polymer insert in the metering zone*
- Page 2 *delete* lines 23 to 29 *insert* BICC Limited. The homogenising zone is described and claimed in the Applicant Maillefer S.A.'s British Patent No 964428.
- Page 5 *delete* lines 12 to 21
- Page 5 *for* claims 2 to 11 *read* 1 to 10
- Page 5, line 37 *delete* or Claim 2
- Page 5, line 40 *delete* any one of the preceding claims *insert* Claim 1 or Claim 2
- Page 5, line 47 *for* 4 *read* 3
- Page 5, line 51 *for* 4 and 6 *read* 3 and 5
- Page 5, line 54 *for* 4 and 6-7 *read* 3 and 5-6
- Page 5, line 65 *for* 10 *read* 9
- Page 6 *for* claims 12 to 16 *read* 11 to 15
- Page 6, line 14 *for* 14 *read* 13

THE PATENT OFFICE
11 June 1979

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amounts of water should not normally be present, and in particular cases a superheated operation may be necessary. If necessary

ERRATUM

Slip No 2

SPECIFICATION NO 1526398

Page 15 *delete* B. F. TARBOX *insert* R. F. TARBOX

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(54) MANUFACTURE OF EXTRUDED PRODUCTS

- (71) We, BICC LIMITED (formerly British Insulated Callender's Cables Limited), a British Company of 21 Bloomsbury Street, London WC1B 3QN, and ETABLISSEMENTS MAILLEFER S.A., a Swiss Body Corporate of CH-1024 Ecublens, Lausanne, Switzerland, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:-
- This invention relates to the manufacture of extruded products, especially but not exclusively electric cables and pipes, that are of carbon-chain polymers cross-linked by the use of hydrolysable unsaturated silane. Such products are formed by first reacting the polymer with the hydrolysable unsaturated silane in the presence of a free-radical generator, such as a peroxide, and afterwards exposing the grafted material to the effects of moisture and a silanol condensation catalyst. Suitable reagents have been described in the specification of British Patent No. 1286460. It is now known, however, that the process is applicable to a variety of polymers other than polyethylene and the modified polyethylenes referred to in that specification, for example chlorinated polyethylenes and a wide range of olefin copolymers can be processed, and in the practice of the present invention the reaction conditions set forth need not in all cases be strictly adhered to.
- Hitherto the manufacture of extruded products by the hydrolysable unsaturated silane cross-linking technique has been a three-stage process: first the grafted polymer is prepared, secondly it is shaped, and thirdly the shaped article is cured. Usually the catalyst is incorporated in the second stage, although it has been suggested that it could be introduced before or during the grafting reaction.
- In accordance with the invention, a method of making a cross-linked extruded product comprises: metering into a screw extrusion machine polymer capable of being cross-linked by the use of hydrolysable unsaturated silane together with compounding ingredients comprising a hydrolysable unsaturated silane, a free-radical generator and a silanol condensation catalyst; blending the compounding ingredients with the polymer in the barrel of the said extruder and raising the temperature sufficiently to effect grafting of silane groups to the polymer, the amount of free-radical generator being sufficiently low (having regard to the other materials present and to other relevant conditions) to limit direct free-radical cross-linking to a level that will not prevent extrusion of the material; extruding the reaction mixture from the said extruder through an extrusion die to form an elongate shaped product; and cross-linking the grafted polymer in the shaped product by the action of moisture. The scrupulous exclusion of moisture from the materials fed to the extruder is not required, but, as in conventional extrusion processes, large amounts of water should not normally be present, and in particular cases a specific drying operation may be necessary. If required, cross-linking can be effected at a temperature below the softening point of the grafted polymer so as to avoid a risk of distortion.
- Other compounding ingredients may be added, for example antioxidants, fillers and pigments. For processing of olefin polymers, the preferred compounding ingredients are vinyl tri-methoxy silane, a peroxide that decomposes rapidly at the grafting temperature, and dibutyl tin dilaurate, but in suitable circumstances any of the alternative reagents listed in the said British Specification No. 1286460 may be used. Preferred peroxides are dicumyl peroxide and 1,3 bis (*tert*butyl peroxy isopropyl) benzene (sold under the trademark Perkadox 14).
- Preferably, the polymer and at least some of the compounding ingredients are metered into and premixed in the hopper of the extruder. Suitable apparatus is commercially available, for example from Colortronic Reinhard & Co. K-G of 6382 Friedrichsdorf/Taunus 2, Otto-Hahn-Strasse 18-20, German Federal Republic, and comprises a hopper with a central powered screw mixer and a

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SEE ERRATA SLIP No. 2

number of digitally controlled metering devices; for metering solid materials, a rotor having a series of metering chambers filled from above and discharging downwards at a separate station is controlled to rotate, usually discontinuously, at the required rate, whereas for liquids an adjustable diaphragm metering pump is used.

5 If the number of compounding ingredients required makes it necessary, or if desired, suitable compounding ingredients may be pre-mixed with the polymer or with each other and metered as a mixture; for example peroxide may be fed as a masterbatch, or as a coating on particles of polymer or filler; the condensation catalyst may usually be dissolved in a liquid silane and metered as a solution; and some fillers that are difficult to disperse, notably conductive carbon black, may 10 be better predispersed in the polymer or some of it. Provided that satisfactory mixing can be achieved, it may be desirable not to add certain ingredients, mostly liquids, to the top of the extruder hopper, but to inject them to the base of the hopper or direct to the throat of the extruder. This applies in particular to ingredients that evolve unpleasant vapour and/or cause the material to stick to the hopper equipment, notably many of the silanes.

15 The extruder itself has a single barrel with at least one screw extending from end to end of it; usually only one screw will be used, but may involve sections with different profiles, possibly including intermediate sections without helical flights (as for example in two stage vented extruders), and the use of intermeshing screws over part or of all of the length is not excluded. On the other hand the use of two or more screws in series is outside the scope of this application even 20 if they operate in integrally connected barrels, except in the case in which the screws operate in the same barrel and are directly mechanically coupled to each other, rigidly or otherwise; in this connection attention is drawn to copending British Application No. 39606/75 of the Applicant BICC Limited. The extruder will ordinarily need to provide a premixing zone, a homogenising zone and a metering zone. Preferably the homogenising zone is of the kind, described and claimed in the Application Mallefer S.A.'s British Patent No. 964428, in which the material to be extruded 25 is forced over the flight of the extruder screw from a converging groove to another groove, not otherwise communicating with the converging groove, one advantage of this arrangement being that entrainment of insufficiently-softened particulate material is inhibited. When the three zones referred to are present, the grafting reaction will normally take place in the metering zone.

30 From the metering zone of the extruder the homogenised and grafted mixture passes to the extruder die, which will normally be mounted in a cross-head in the case of cable manufacture. The finished product can be cross-linked by exposure to water or a moist atmosphere at a suitable temperature, as in the known three-stage silane grafting technique.

35 The method of the invention avoids the need for two high-temperature processing steps and for storing moisture sensitive intermediates such as grafted polymer, whilst retaining the advantage of the silane grafting technique that the extruded product can be examined for dimensional accuracy in a very short period compared with vulcanising and chemical cross-linking methods that involve high-temperature treatment of the extruded product under pressure to effect cross-linking. In addition, it has been found that a higher cross-link density can be achieved than is normally 40 observed in the conventional three-step hydrolysable unsaturated silane technique; this may perhaps be associated with the elimination of ungrafted polymer conventionally used to masterbatch the catalyst.

In the following examples, where physical properties of extruded materials are specified, these are based on measurements in a typical actual test; the results obtained vary appreciably with the 45 detailed design of the extrusion screw.

Example 1

50 Polyethylene with a density of 0.918 and a melt flow index of 2, sold by Imperial Chemical Industries Ltd., under the trademark Alkathene and reference No. WJG47 was fed to the hopper mixer of an extrusion machine together with the following metered amounts of additives (expressed in parts by weight per hundred parts of the polyethylene (phr):

50	Carbon black MB	2.5	50
	Dicumyl peroxide	0.1	
	(added as Perkadox BC40 which is 40% active peroxide but calculated on the basis of the actual peroxide content.)		
55	Vinyl trimethoxy silane (VTMOS)	1.5	55
	Polymerised trimethyl dihydro-quinoline		
	(sold under the trademark Flectol H)	0.5	
	Dibutyl tin dilaurate (DBDTL)	0.05	

60 The extruder screw had an overall length: diameter ratio of about 30:1 and provided a feed zone with a length of about 8 diameters in which the cross section of the passage slowly decreases, followed by a homogenising zone of the kind subject of British Patent No. 964428 occupying about six diameters in which, after an initial expansion, the material is forced over the flight of the screw from a rapidly-converging blind passage into a very slowly converging passage. This is followed by a slightly converging zone of about six diameters and finally a metering zone of 65 uniform cross-section occupying the last ten diameters of the length of the screw.

The barrel of the extruder was maintained at a temperature of 130°C up to and including the homogenising zones and part of the slightly converging section that follows it, and at 230°C for the remainder of its length, including a cross-head by which the extruded material was applied to a wire. To ensure good draw-down, a higher degree of vacuum is needed at the point of the cross-head than would be the case for extrusion of ordinary thermoplastic polyethylene.

The insulation produced had the following typical properties after curing for 16 hours in water at 90°C:

	Gel content	77%	
	Ultimate tensile strength	13 MN/m ²	
10	Elongation at break	270%	10
	Hot-set at 150°C and 0.2 MN/m ² :		
	extension	35%	
	set	-5%	

Example 2

This was similar to Example 1 except that the peroxide was added in 98% active form and its level was reduced to 0.08 phr. Typical properties of the insulation product were:

	Gel content	71%	
	Ultimate tensile strength	12 MN/m ²	
20	Elongation at break	350%	20
	Hot set at 150°C and 0.2 MN/m ² :		
	extension	110%	
	set	+5%	

Examples 3-7

Example 3 was similar to Example 1 except that the peroxide and carbon black were masterbatched with a small amount of additional polyethylene.

Examples 4-7 were similar to Example 3 except that the DBTDL was replaced by the same weight of an alternative catalyst as follows: Example 4, dibutyltin dimaleate; Example 5, Stanciere T86; Example 6, Stanciere T186; and Example 7, Advastab T36 (the words Stanciere and Advastab being trademarks and the materials being available on the open market).

Typical properties of the insulation produced in these examples were as follows:

Example	3	4	5	6	7	
Gel content	73	70	70	68	69	%
Ultimate Tensile Strength	16	15	17	14	15	MN/m ²
Elongation at Break	380	530	580	380	440	%
Hot Set 150°C and 0.2 MN/m ² :						
Elongation	60	70	95	70	85	%
Set	nil	nil	nil	nil	nil	%

Example 8

This was similar to Example 3 except that the VTMO content was reduced to 1 phr.

	Typical properties of the insulation produced were as follows:		
	Gel content	65%	
45	Ultimate Tensile strength	15 MN/m ²	45
	Elongation at break	530%	
	Hot set: elongation	110%	
	set	-5%	

Examples 10-12

These were similar to Example 1 except that the VTMO content was raised to 2.0 phr in Examples 10 and 12, and carbon black omitted in Example 12 and the VTMO content was raised to 2.5 phr in Example 11, the peroxide in Example 12 being added in the 96% active form sold under the trademark Perkadox SB.

Typical properties of the insulation produced were as follows:

Example	10	11	12	
Gel Content	81	79	78	%
Ultimate Tensile Strength	16	14	14	MN/m ²
Elongation at Break	350	260	300	%
Hot Set 150°C and 0.2 MN/m ²				
elongation	55	25	35	%
set	nil	-5	-2.5	%

Examples 13-14

These were similar to Example 12 except that i) the peroxide content was increased to 0.15 phr and 0.265 phr respectively and ii) the extrudate was produced in pipe form and iii) cured for 6 hours in boiling water. Typical properties of the extruded material produced in these examples were as follows:

Example	13	14		
Gel Content	83	83	%	
Vicat Penetration 140°C	0.54	0.33	mm	
Ultimate Tensile Strength	12.6	12.5	MN/m ²	
Elongation at Break	280	245	%	
Hot Set 138°C and 0.2 MN/m ²				
Elongation	40	32	%	
Set	nil	nil	%	

Note: The Vicat test reported in this and subsequent examples is different from the British Standard Recommendation. A load of 100g weight was applied by a circular flat indenter with an area of 2 mm² and penetration measured after 10 minutes at 140°C.

Example 15

This was similar to Example 14 except that the polyethylene was that sold as Alkathene XNM-68, having a density of 0.924, and a melt-flow index of 8. Typical properties of the extruded material were as follows:

Gel Content	79%
Vicat Penetration at 140°C	0.56 mm
Yield Stress	11 MN/m ²
Ultimate Tensile Stress	14 MN/m ²
Elongation at Break	265%
Hot Set 138°C and 0.2 MN/m ² :	
Extension	39%
Set	nil

Example 16

This was similar to Example 15 except that the polyethylene was that sold by Bakelite Xylonite Ltd., as grade PN-220. This is supplied containing carbon black, the density of the material as purchased (which should be distinguished from that of the base polymer therein) being 0.930 and its melt flow index 0.12. Typical properties of the extruded material were as follows:

Gel Content	79%
Vicat Penetration 140°C	0.45 mm
Yield Stress	9.6 MN/m ²
Ultimate Tensile Stress	15 MN/m ²
Elongation at break	340%
Hot set 138°C and 0.2 MN/m ² :	
extension	41%
set	2½%

Examples 17-18

Example 17 was similar to Example 16 except that the content of the peroxide was reduced to 0.15 phr. Example 18 was similar to Example 17 except that the content of peroxide, silane and catalyst were all reduced by half. Typical properties of the extruded material produced were as follows:

Example	17	18		
Gel Content	74	62	%	
Vicat Penetration 140°C	1.1	1.7	mm	
Yield Stress	9	10	MN/m ²	
Ultimate Tensile Strength	16	18	MN/m ²	
Elongation at Break	440	510	%	
Hot Set 138°C and 0.2 MN/m ² :				
elongation	63	70	%	
set	2½	2½	%	

Example 19

This was similar to Example 11 except that the dicumyl peroxide was replaced by 0.25 phr of 1,3 bis (*tert*.butyl peroxy isopropyl) benzene, added as Perkadox 14/96, which has an activity of about 96% and that the insulation was cured for 6 hours in water at 100°C. Typical properties of the extruded material were as follows:

Tensile Strength	13.6 MN/m ²
Elongation at Break	215%
Gel Content	84%

WHAT WE CLAIM IS:

1. A method of making a cross-linked extruded product comprising: metering into a screw extrusion machine a polymer capable of being cross-linked by the use of hydrolysable unsaturated silane together with compounding ingredients comprising a hydrolysable unsaturated silane, a free-radical generator and a silanol condensation catalyst; blending the compounding ingredients with the polymer in the barrel of the said extruder and then raising the temperature sufficiently to effect grafting of silane groups to the polymer, the amount of free-radical generator being sufficiently low to limit direct free-radical cross-linking to a level that will not prevent extrusion of the material; extruding the reaction mixture from the said extruder through an extrusion die to form an elongate shaped product; and cross-linking the grafted polymer in the shaped product by the action of moisture.
2. A method of making a cross-linked extruded product comprising: metering into a screw extrusion machine having in succession a premixing zone, a homogenising zone of the kind in which the material to be extruded is forced over the flight of the extruder screw from a converging groove to another groove not otherwise communicating with the converging groove and a metering zone a polymer capable of being cross-linked by the use of a hydrolysable unsaturated silane together with compounding ingredients comprising a hydrolysable unsaturated silane, a free-radical generator and a silanol condensation catalyst; blending the compounding ingredients with the polymer in the barrel of the said extruder in the mixing and homogenising zones and then raising the temperature sufficiently to effect grafting of silane groups to the polymer in the metering zone, the amount of free-radical generator being sufficiently low to limit free-radical cross-linking to a level that will not prevent extrusion of the material; extruding the reaction mixture from the said extruder through an extrusion die to form an elongate shaped product; and cross-linking the grafted polymer in the shaped product by the action of moisture.
3. A method as claimed in Claim 1 or Claim 2 in which the cross-linking is effected at a temperature below the softening point of the grafted polymer.
4. A method as claimed in any one of the preceding claims in which the polymer and at least some of the compounding ingredients are metered into and premixed in the hopper of the extruder.
5. A method as claimed in any one of the preceding claims in which at least one compounding ingredient is metered as a mixture with the polymer or with another compounding ingredient.
6. A method as claimed in any one of claims 1-4 in which the free-radical generator is a peroxide which is metered as a masterbatch with the polymer or as a coating on particles of polymer or filler.
7. A method as claimed in any one of claims 1-4 and 6 in which a filler is metered as a predispersed mixture with the polymer or some of it.
8. A method as claimed in any one of claims 1-4 and 6-7 in which the condensation catalyst is metered as a solution in a liquid silane.
9. A method as claimed in any one of the preceding claims in which at least one liquid compounding ingredient is injected to the base of the hopper of the extruder or injected direct into the throat of the extruder.
10. A method as claimed in any one of the preceding claims in which the polymer is polyethylene and the compounding ingredients comprise vinyl trimethoxy silane, a peroxide, and dibutyltin dilaurate.
11. A method as claimed in Claim 10 in which the peroxide is dicumyl peroxide.

12. A method as claimed in any preceding claim in which the extrusion machine has a single screw.
13. A method of making a cross-linked extruded product substantially as described with reference to the Examples considered collectively. 5
14. A method of making a cross-linked extruded product substantially as described with reference to any one of the numbered Examples.
15. A cross-linked extruded product made by the method claimed in any one of the preceding claims. 10
16. An electric cable with cross-linked insulation made by the method claimed in any one of claims 1-14. 15
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